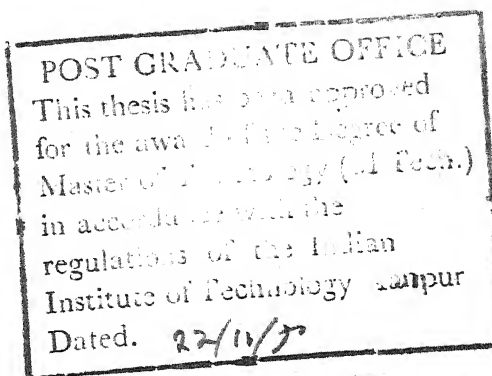


EFFECT OF LIQUID ON GAS FED TO A FIXED BED CATALYTIC REACTOR

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

BY
ANIL KUMAR

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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
SEPTEMBER, 1970

CERTIFICATE

It is certified that this work has been carried out
under my supervision and that this has not been submitted
elsewhere for a degree.

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POST GRADUATE OFFICE
This thesis has been approved
for the award of the degree of
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ABSTRACT

Effect of an inert high boiling phase in a gas phase catalytic reaction was studied. The reaction studied was the vapor phase hydrogenation of benzene over Nickel catalyst on special support and the inert liquid phase present in the feed was n-Butanol. Reaction was studied at 84°, 94°, 104° and 114°C and for butanol feed rates of .02 and .2 ml/min. The liquid benzene flow rate was 0.1 ml/min. and hydrogen rate was 78 ml/min. The product of reaction was analysed by VPC using a 10 ft. long carbowax 10% column. It was observed that the reaction rate dropped with time. Chemisorption of butanol and condensation of butanol in the pore were given as probable causes.

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CHAPTER I

INTRODUCTION

In a fluid solid catalytic reaction, the following steps occur sequentially in converting reactants into products:

1. Diffusion of reactants from bulk phase to catalytic surface,
2. Adsorption of reactants at active sites on the catalyst surface,
3. Reaction on the catalyst surface,
4. Desorption of reaction products, and
5. Diffusion of desorbed products from the catalyst surface into the bulk stream.

With porous catalysts internal diffusion through the pores of the catalyst may be involved as well as external diffusion (steps 1 and 5) in the fluid phase surrounding the catalyst particle. Some of the reactant molecules, for example, will not be adsorbed on the outer surface of the catalyst but will diffuse into the pores and be adsorbed and react on the internal pore surface. In such cases two additional steps should be added to the list: (1a) internal diffusion of reactants along the pores; (5a) internal diffusion of the products along the pores to the outer surface.

Processes 1 and 5 can be handled independently of the others. However, the internal-diffusion steps (1a) and (5a) cannot be separated from the surface reactions 2, 3 and 4.

We are interested in the fluid solid reactions in which the feed consists of both the gaseous and liquid phases. Slurry reactions and trickle bed reactors are examples of the fluid-solid reactions in which one of the reacting phases is vapor and the other reacting phase is liquid.

Reactions in which the liquid phase does not take part into the reaction and remains as an inert are common in petrochemistry. Here the gaseous feed to a heterogeneous reactor consists of high boiling inerts which condense over the catalyst bed. For example in the hydrogenation of catalytic cracking charge stocks (1), most catalytic cracking charge stocks have relatively low volatilities and thus are only partially vaporized under normal hydrogenation conditions. Under such conditions, mass transfer rates may be controlling for some reactions. The effect of this condensate over the activity of the catalyst is the problem under study. It was proposed to find out how is the catalyst activity affected with the presence of high boiling inert in the feed. Does the activity remain unaltered or drop down or is the catalyst poisoned and spoiled?

The vapor phase hydrogenation of benzene in a fixed bed catalytic reactor was chosen as the reaction for study. n-Butanol was selected as the high boiling inert component in the feed.

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CHAPTER II

LITERATURE REVIEW

Almost no mass transfer data are available in three phase reactions where mass transfer of gases are through liquid films. Babcock, et al. (2), hydrogenated α -methyl styrene in a trickle bed of palladium-on-alumina pellets, but the chemical rate, and not mass transfer, was shown to be controlling at rates in the range .005 to .03 gm. moles/hr.gm.cat. using hydrogen pressure of 2 to 12 atm. at 27°C. Miller hydrogenated cottonseed oil on Ni catalyst in a trickle bed reactor and found that the mass transfer resistance was negligible. Similar conclusion was drawn by Klassen who air-oxidized ethanol to acetic acid over Palladium catalyst and reported that the rate controlling step was the surface reaction. On the other hand, in case of the hydrogenation of catalytic cracking charge stock the mass transfer resistance was found to be appreciable (1). A significant fraction of the catalytic cracking charge stock has relatively low volatility and thus it is only partially vaporized under normal hydrogenation conditions. Under such conditions, catalyst pores may be filled with unvaporized liquid fraction and mass transfer rates may be controlling the reaction. Slow surface reactions are less affected by diffusion limitations in comparison to fast surface reactions.

Diffusion effects are difficult to isolate in mixed

phase, solid catalysed, reaction studies. Most published work on the hydrogenation conversion report combined diffusion and surface reaction effects. The factors which increase turbulence and reduce the quantity of liquid present in the reactor will increase overall conversion by reducing diffusional resistance.

Catalyst pore diameter, pore size distribution, and particle size will influence diffusion rates to and from the catalyst surface. Thus, they are important only in processes in which resistance to diffusion is major in the overall reaction process. In the hydrogenation of benzene to cyclohexane, Burke et al.(3) found that decreasing catalyst particle size down to a limiting value resulted in higher rates of reaction. It was hypothesized that decrease in particle size reduced the mass transfer limitations to the catalyst surface inside the pores until such a degree of subdivision was reached that diffusion limitation through pores was no longer significant. Ware~~o~~found that the rate of diffusion is significant in the overall rate during mixed phase hydrogenation of benzene in a trickle reactor. It was also shown that the rate of diffusion through gaseous films is much greater than through corresponding liquid film. In the mixed phase reactor, hydrogen is the limiting reactant at the catalyst surface even though there may be a large overall excess of hydrogen. Since the rate of hydrogen diffusion is slow through liquid hydrocarbons, catalyst sites

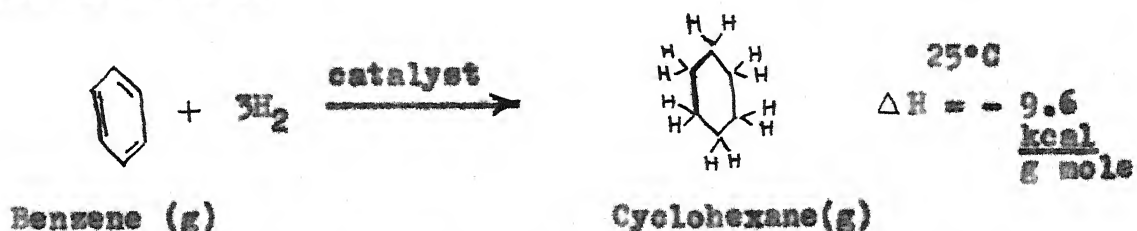
in pores filled with liquid will be ineffective for catalyzing the hydrogenation reaction. Internal pore surfaces would be expected to be much more effective in vapor-phase reactions, however. Thus in catalytic hydrogenation processes, reaction velocity increase is to be expected by decreasing catalyst particle size and by operating in such a way as to reduce the possibility of liquid collection at the catalyst surface and in the catalyst pores.

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CHAPTER III

VAPOR PHASE HYDROGENATION OF BENZENE

The system chosen for study is the vapor phase hydrogenation of benzene. Benzene undergoes hydrogenation over a variety of catalysts, and this reaction provides a very convenient method to test the catalytic activity. The hydrogenation proceeds cleanly to cyclohexane unless elevated temperatures (above 350°C) are employed when side reactions like cracking and rearrangement into a variety of products become important. The stoichiometry of benzene hydrogenation is given as follows:



At room temperatures benzene may be reduced over Platinum, Palladium and similar catalysts. In general, elevated temperatures are required for reduction of benzene with hydrogen over such material as Nickel, Copper and Cobalt.

The mechanism for the hydrogenation of benzene, particularly on Pt and Ni, has been the subject of considerable discussion. In general, the reaction is zero order with respect to benzene and first order with respect to hydrogen either in gas or liquid phases (4), although exceptions have been reported. For instance Herbo (5) found that with Nickel catalysts at atmospheric pressure in a flow system

the reaction is zero order with respect to benzene and first order with respect to hydrogen upto around 180°C while at higher temperatures the reverse is true. This change in order probably suggests that the benzene molecule is more strongly adsorbed than hydrogen at low temperatures, but the relationship is reversed at higher ones.

It is difficult to distinguish between the two possibilities for the mechanism of benzene hydrogenation. According to one mechanism known as adjacent interaction mechanism, two reacting molecules are adsorbed on adjacent sites in a chemisorbed monolayer and, after interaction in the monolayer, the product is desorbed. Herbo (6) interprets the hydrogenation of benzene over a Nickel catalyst promoted with ZnO and Cr_2O_3 as taking place between adjacent adsorbed molecules, and suggests that these sites are located at the interface between the promoter and the Nickel surface.

The second possibility is that one reacting species is chemisorbed on the catalyst surface and molecules of the other species react with it from the gas phase or van der Waals layers. This mechanism has been called van der Waals chemisorbed layer interaction.

In the present study supported nickel catalyst was used. Normal butanol was used to provide an inert liquid phase in reaction system.

* * *

CHAPTER IV

EXPERIMENTAL SET-UP AND PRODUCT ANALYSIS

Figure 4.1 shows the schematic diagram of the experimental set-up. A general description of the set-up is given below, followed by details of the reactor, catalyst, and analysis of the product.

The commercial grade hydrogen from high pressure gas cylinder was used. Differential manometer was used to indicate the pressure drop across the capillary and was calibrated in terms of flow rate. Hence it was possible to maintain H_2 gas at the required flow rate by adjusting the needle valve. Liquid benzene was pumped by liquid metering pump (Beckmen type, 0-5 ml). Liquid benzene and hydrogen were mixed and passed through the vaporizer tube. Vaporizer tube was heated electrically at a voltage of 15V. The outcoming mixture of hydrogen and benzene vapors was mixed with liquid n-butanol and fed to the reactor kept in the constant temperature bath. The n-butanol was pumped using a liquid metering pump (Beckmen type, 0-5 ml). The liquid in the bath was water, for temperatures below $100^\circ C$, and crude glycerol, for temperatures above $100^\circ C$. The bath had built-in temperature control system of an accuracy of $\pm 1^\circ C$. The liquid in the bath was constantly stirred to insure a uniform temperature.

The product from the reactor was condensed in the ice traps and taken out from time to time for analysis.

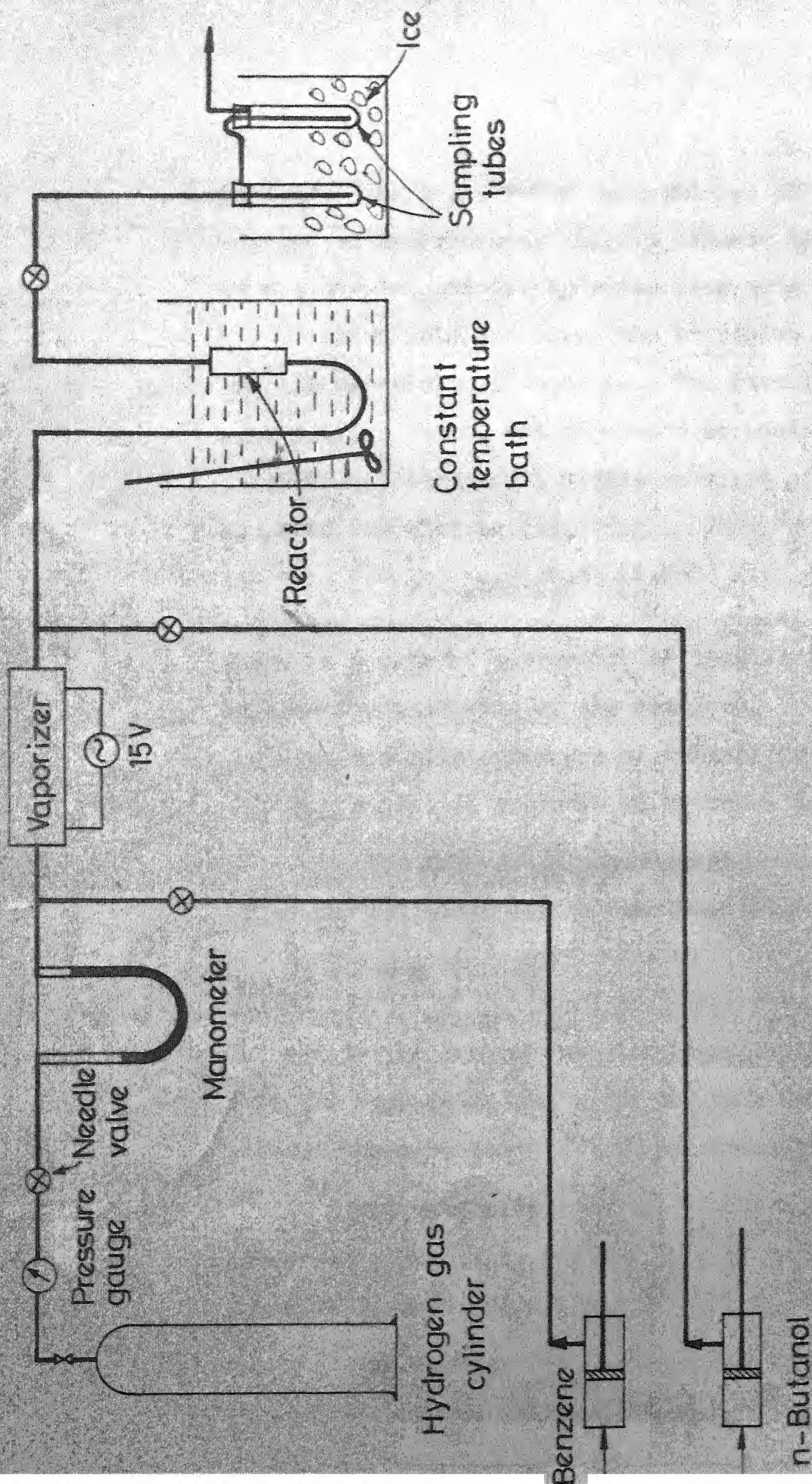


Fig.4.1 - Schematic diagram of the experimental setup.

Reactor: The reactor was designed for 50% conversion of benzene to cyclohexane. Liquid benzene feed rate was fixed at 0.1 ml/min. and the hydrogen flow rate was kept at 78 ml/min. The hydrogen rate was twice the stoichiometric requirement for 50% conversion of benzene. The Nickel catalyst was analysed for Nickel and was found to contain 4.5% of Nickel. The rate equation for a Nickel catalyst of this composition has been reported as (7),

$$r = .096 p_B^{0.3} p_{H_2}^{1.6}$$

where r = rate of conversion of benzene to cyclohexane defined for unit mass of the catalyst,

p_B = partial pressure of benzene in feed,

p_{H_2} = partial pressure of hydrogen in feed.

The mass of catalyst needed was calculated by using the following design equation (8),

$$\frac{W}{F} = \int_0^x \frac{dx}{r_c}$$

where W is the mass of the catalyst, F is the feed rate, x is the conversion and r_c is the rate defined as mass of product produced per unit mass of catalyst per unit time.

The integration in the above design equation was performed graphically and the mass of catalyst needed was found to be equal to 7.2 gms.

The reactor was designed for 100% excess volume. It was made of 0.6 inch inside diameter stainless steel tube. The detailed mechanical design of the reactor is

given in Figure 4.2.

Catalyst: The catalyst available was in the form of nickel oxide, NiO. The oxide was deposited on special porous support and was in shape of cylindrical pellets of $1/8"$ x $1/8"$ dimensions. It was necessary to reduce the catalyst before it could be used for the hydrogenation. The reduction was carried out in a bulb of the type shown in Fig. 4.3. The bulb was electrically heated from outside and the catalyst pellets were reduced by passing hydrogen. The reduction was carried out at 350-400°C by supplying 60V (A.C.) to the heater for 3.5 hrs. Hydrogen was passed at 80 ml/min.

Regeneration before each run was done by externally heating the reactor electrically at a temperature of about 200°C for 4 hours.

Analysis of the Product: Product from the reactor contained benzene, cyclohexane and n-butanol. The analysis was done by vapor phase chromatography using a 10 ft. long, 10% carbowax, column. The oven temperature was maintained at 80°C. Detector and injector temperatures were kept at 110°C and 140°C, respectively. Sample injected was 1 μ l. Hydrogen at 40 cc/min. was used as a carrier gas. Under the above operating conditions, the retention times for cyclohexane, benzene and n-butanol were 20 seconds, 39 seconds and 2 minutes 13 seconds respectively. The column gave very good separation and peaks for benzene and cyclohexane but was relatively less sensitive towards n-butanol.

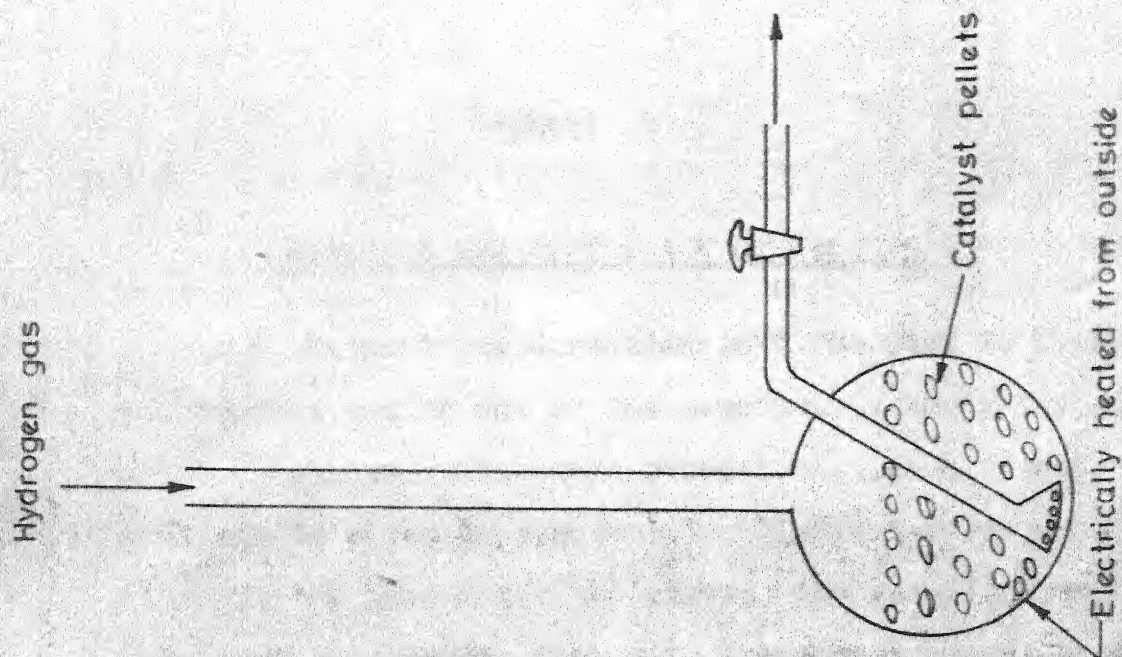


Fig.4.3 - Glass bulb used for reducing the oxide catalyst.

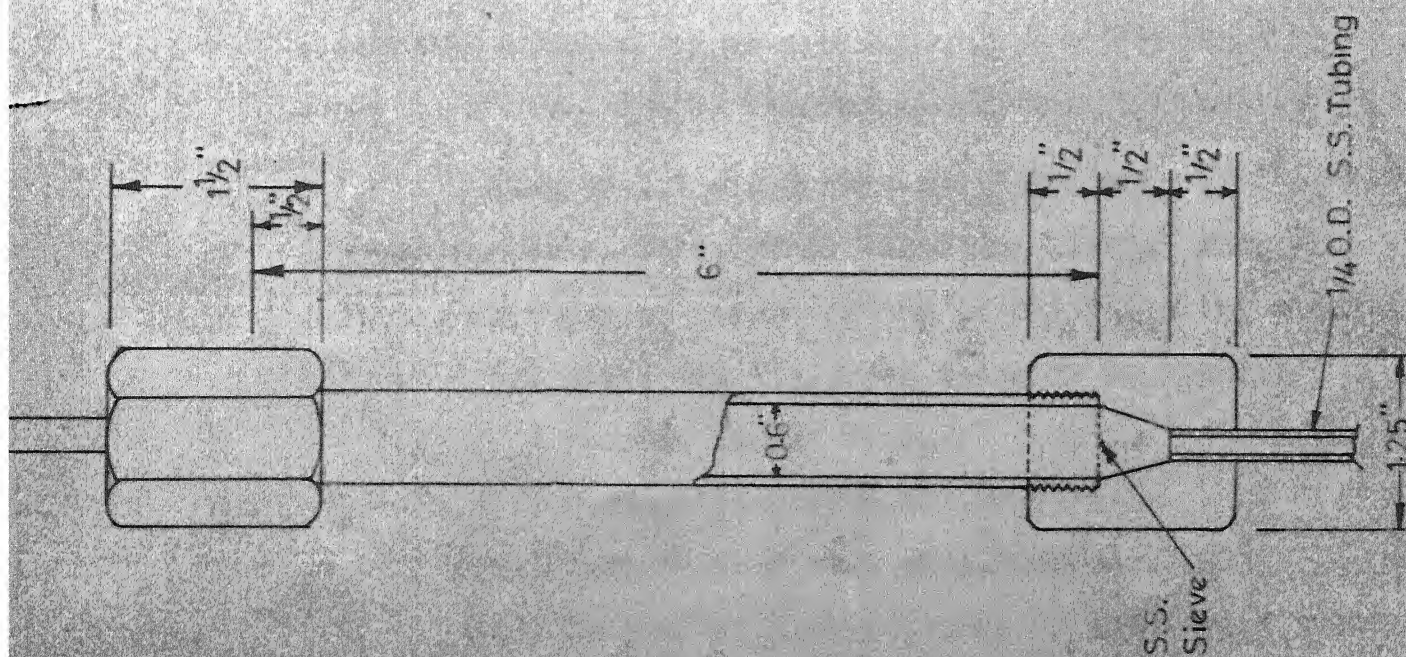


Fig. 4-2 - Stainless Steel Reactor.

CHAPTER V

ANALYSIS AND DISCUSSION OF RESULTS

Vapor phase chromatography was used to analyse the product coming out of the reactor. A typical chromatogram of benzene-cyclohexane-butanol mixture obtained during analysis is shown in Figure 5.1. Planimeter was used to find out the area under the curve. The results have been tabulated in Appendix A showing the percentage of benzene converted to cyclohexane at different time intervals and at four temperatures. As the activity of the catalyst before the start of each run was never the same, the conversions at different time intervals were divided by a hypothetical conversion obtained by extrapolating the conversion-time curve to a time, $t = 0$. This ratio has been denoted by $\frac{X(t)}{X(0)}$.

Figures 5.2 - 5.5 give the $\frac{X(t)}{X(0)}$ versus time plot for temperatures, 84°C, 94°C, 104°C and 114°C. Each plot contains five curves corresponding to the following conditions:

- (i) Blank run i.e., when there is no butanol present in the feed.
- (ii) Butanol feed rate of .02 ml/min.
- (iii) Butanol feed rate of 0.2 ml/min.
- (iv) Rate of filling of pores by condensing butanol at butanol feed rate of .02 ml/min.
- (v) Rate of filling of pores by condensing butanol at butanol feed rate of 0.2 ml/min.

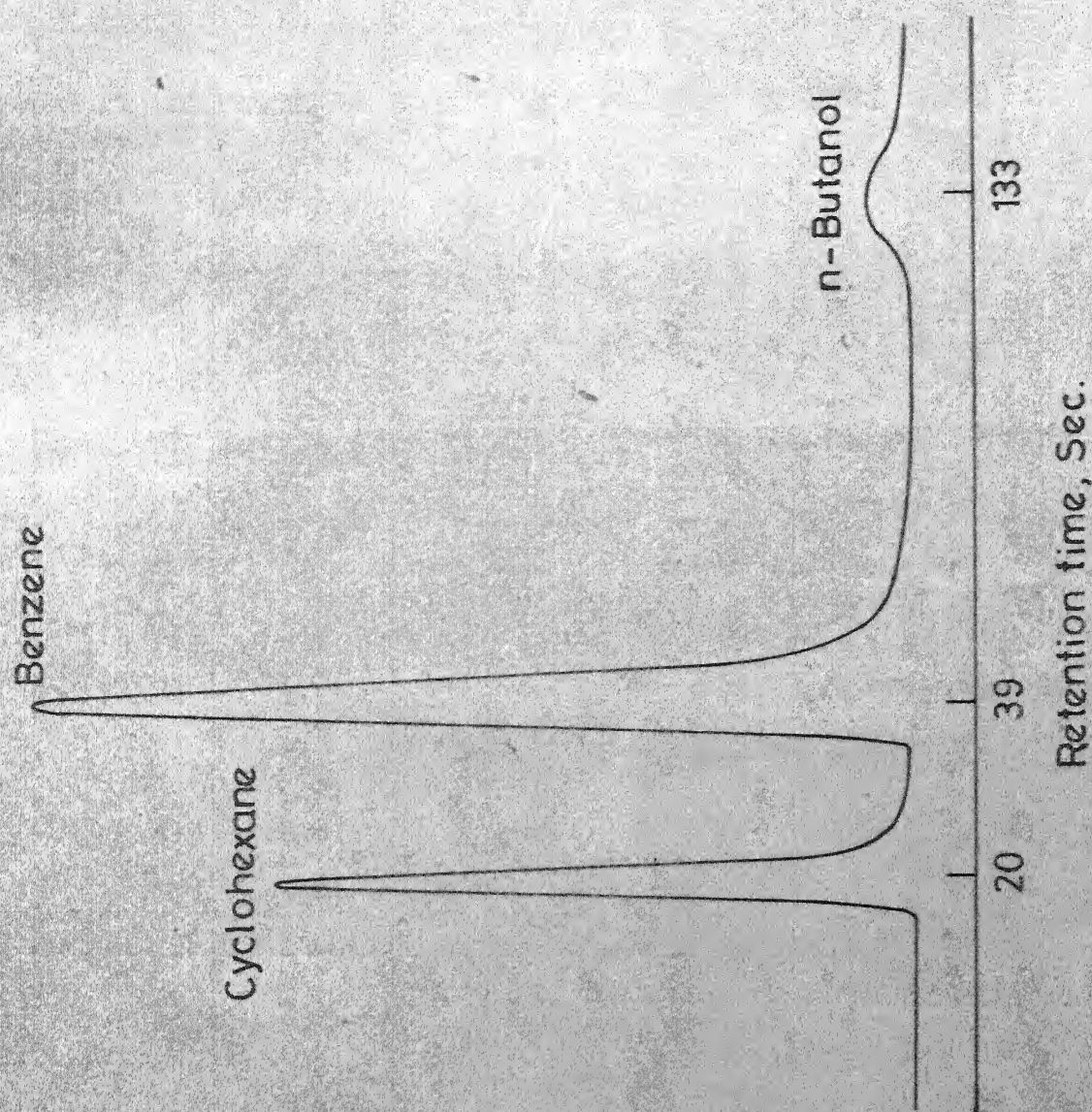


Fig. 5.1 - A Chromatogram of the product showing cyclohexane, benzene and n-Butanol peaks.

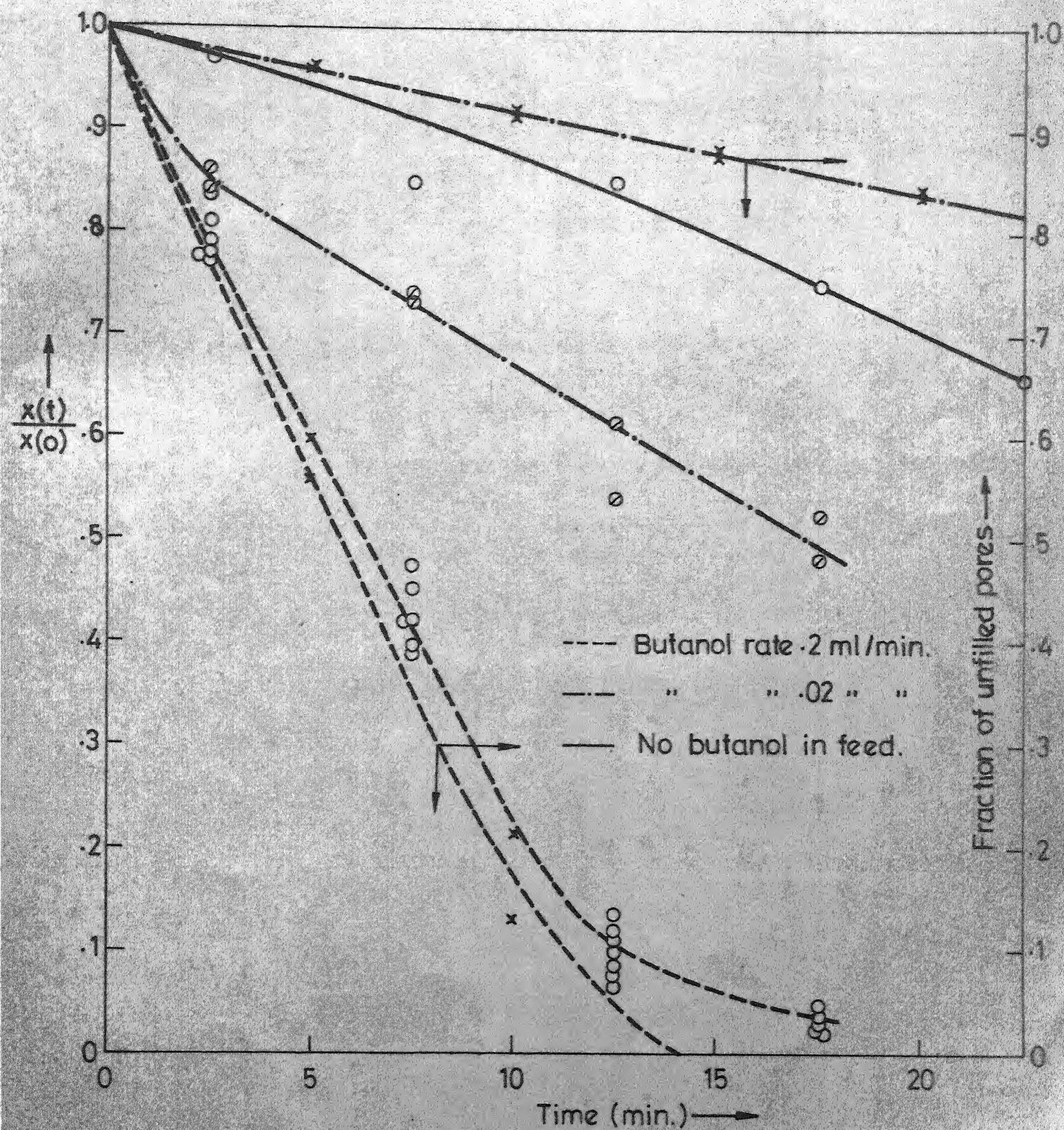


Fig.5.2-Plot of $\frac{x(t)}{x(0)}$ and fraction of unfilled pores with time.
 Temp. 84°C

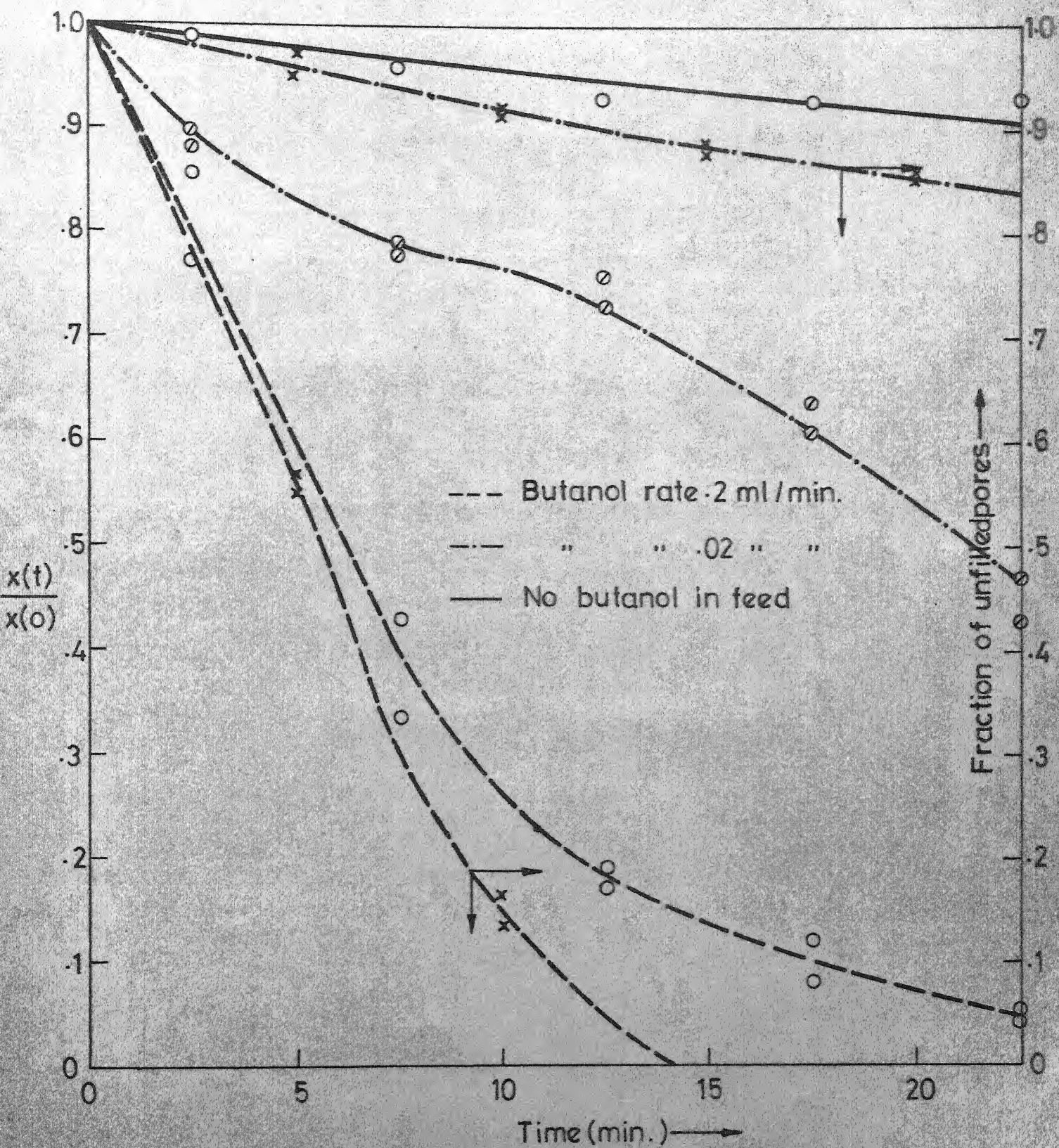


Fig.53- Plot of $\frac{x(t)}{x(0)}$ and fraction of unfilled pores with time.
Temp.94°C.

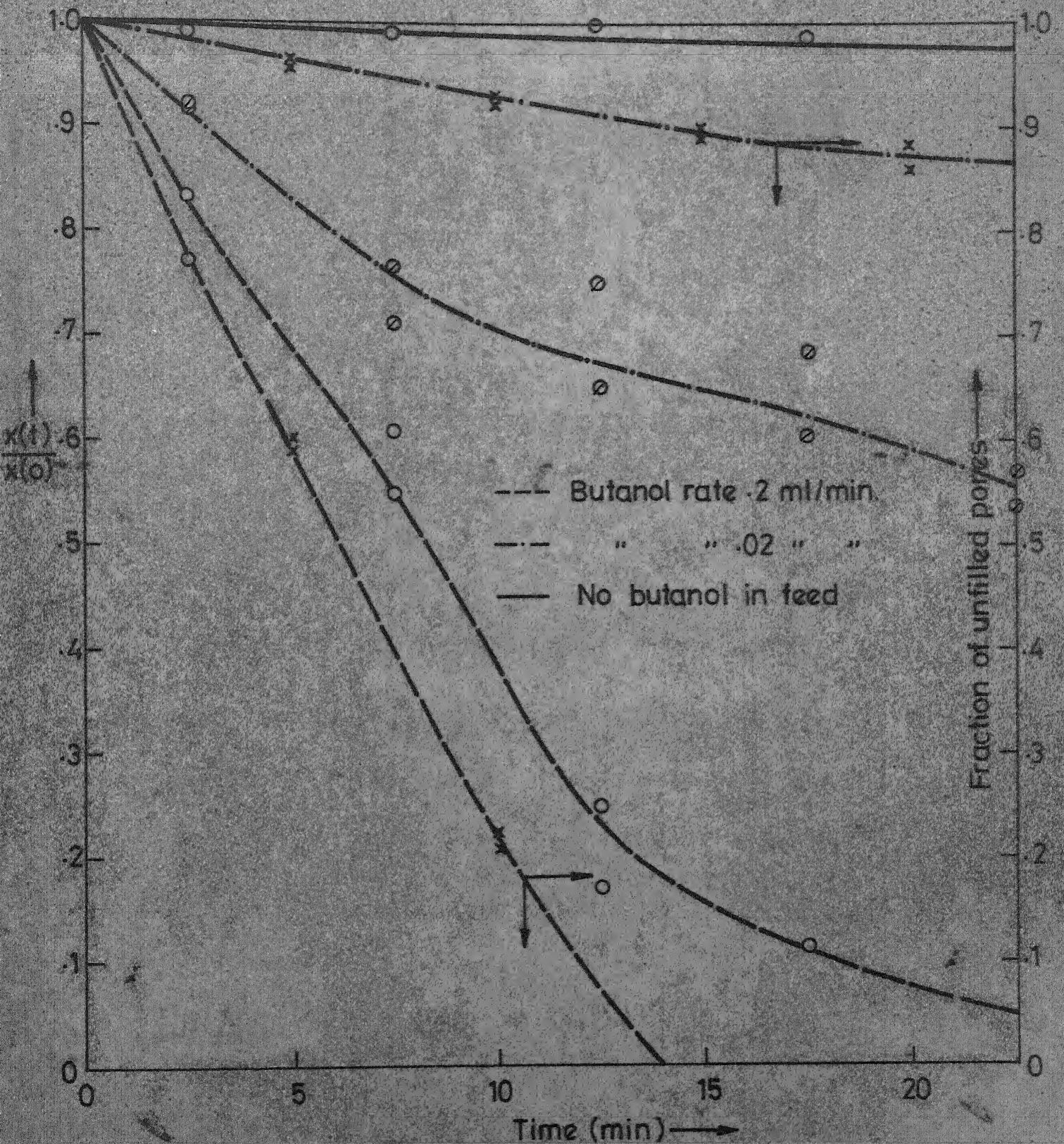


Fig.5-4-Plot of $\frac{x(t)}{x(0)}$ and fraction of unfilled pores with time.
Temp. 104°C.

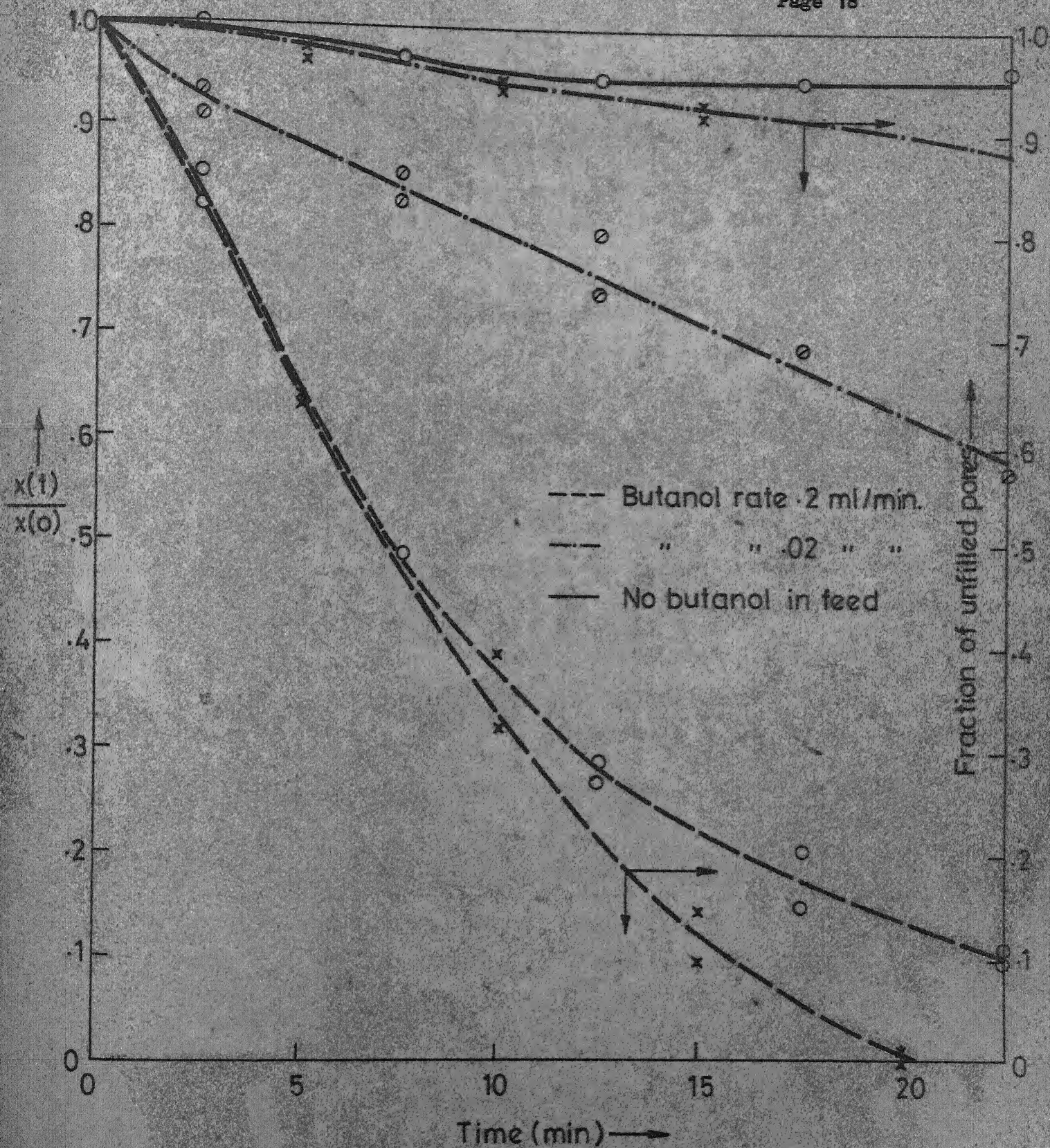


Fig.5.5- Plot of $\frac{x(t)}{x(0)}$ and fraction of unfilled pores with time.
Temp. 114°C.

Rate of condensation of butanol was obtained by dividing the volume of butanol retained in the bed by the total pore volume.

The curves in Figures 5.2 - 5.5 show a decrease in reaction rate with time. The general nature of the curves is the same at all the four temperatures.

An analysis of the product stream shows that the butanol contained in the product is lesser than the butanol in feed. The amount of butanol retained in the bed has been calculated with the help of material balance. The fraction of pores filled at various time intervals has been calculated with the assumption that all the butanol retained in the bed condenses in the pores. Tables in Appendix B give the fraction of pores filled with time. This has been plotted on the reaction rate versus time plot (Figures 5.2 - 5.5).

At 84°C (Fig. 5.2) the blank run shows a considerable drop in conversion with time. This is perhaps because of the condensation of benzene in very fine pores. The drop in reaction rate at butanol rate of 0.2 ml/min. is very rapid and is very close to the rate curve corresponding to the filling of capillaries. This probably indicates the butanol condensation in the pores. The same phenomenon is repeated at the butanol feed rate of .02 ml/min. but here the reaction rate curve falls below the rate of capillary filling curve. This indicates that there is some other factor causing the drop in reaction rate besides the probable butanol condensation.

Chemisorption of butanol can be the other factor responsible for drop in reaction rates. The chemisorption of butanol shall result in reduction of number of available active sites which in turn shall result in reduction of reaction rate. This hypothesis is supported by the fact that alcohols readily chemisorb on Nickel surface.

The nature of reaction rate curves at other temperatures, for butanol feed rate of .02 ml/min. can similarly be explained in the light of butanol condensation combined with chemisorption of butanol.

An attempt was made to support the possibility of butanol condensation by the use of Kelvin equation (Appendix C) without much success. The results indicated complete filling of the pores only at 84°C and .2 ml/min. butanol rate. For the same butanol rate, at 94°C, the calculation indicated partial filling of the pores (pore upto a radius of 17.3 \AA filled). At higher temperatures the calculations indicated practically no filling of pores. At the butanol feed rate of .02 ml/min. the Kelvin equation calculations predicted practically no filling of pores at any of the temperatures.

However, as we do not know the pore size distribution for the catalyst sample used, the results obtained from Kelvin equation fail to give us any information about the percentage of pores filled. Secondly, the Kelvin equation used is based on the assumption of cylindrical pores.

Inspite of the above deficiencies the results give us an insight in the complexity of the situation. The

results almost rule out the possibility of condensation of butanol in the pores.

The foregoing discussion indicates that the drop in the reaction rate is probably because of mixed phenomenon of chemisorption of butanol and condensation of butanol in the pores. In view of the various uncertainties in the data and analysis, it is not possible to draw definite conclusions about the factors responsible for the drop in reaction ~~rate~~ rate. However, the analysis does give a qualitative picture of the effect of the inert liquid on the gas phase reaction.

* * *

B. Butanol Flow Rate = 0.2 ml/min.

Set No.	Product Composition (Mole %)	Time (Minutes)			
		5	10	15	20
1	C ₆ H ₁₂	32.5	17.9	3.7	0.8
	Benzene	56.9	65.6	69.7	68.9

	Benzene hydro- genated (butanol free basis)	36.4	21.4	5.05	1.2
	$\frac{x(t)}{x(0)} = \frac{x(t)}{45}$.81	.48	.11	.03
2	C ₆ H ₁₂	39.5	17.9	3.66	0.8
	Benzene	50.5	63.4	68.4	67.8

	Benzene hydro- genated (butanol free basis)	44	22	5.1	0.9
	$\frac{x(t)}{x(0)} = \frac{x(t)}{52.4}$.84	.42	.10	.02
3	C ₆ H ₁₂	23.8	12.1	2.75	0.46
	Benzene	64.2	70.9	75.2	69.5

	Benzene hydro- genated (butanol free basis)	27	14.8	3.5	.7
	$\frac{x(t)}{x(0)} = \frac{x(t)}{35}$.77	.42	.10	.02
4	C ₆ H ₁₂	28.9	13.75	3.8	1.4
	Benzene	58.8	69.8	71.6	28.

	Benzene hydro- genated (butanol free basis)	32.9	16.4	5.05	1.9
	$\frac{x(t)}{x(0)} = \frac{x(t)}{42.5}$.78	.39	.12	.05

Set No.	Product composition (Mole%)	Time (Minutes)			
		5	10	15	20
5	C_6H_{12}	37.1	19	5.6	1.37
	Benzene	52.25	61	71.4	70.6

	Benzene hydrogenated (butanol free basis)	41.6	23.8	7.3	1.9
	$\frac{x(t)}{x(0)} = \frac{x(t)}{52.5}$.79	.45	.14	.04
6	C_6H_{12}	30.3	14.5	2.8	
	Benzene	56.8	67.5	71.2	

	Benzene hydrogenated (butanol free basis)	34.8	17.7	3.8	
	$\frac{x(t)}{x(0)} = \frac{x(t)}{44.9}$.775	.394	.085	
7	C_6H_{12}	29	14.5	2.0	
	Benzene	58.7	64.7	78.8	

	Benzene hydrogenated (butanol free basis)	33.1	18.3	2.8	
	$\frac{x(t)}{x(0)} = \frac{x(t)}{42.5}$.78	.431	.066	
8	C_6H_{12}	31	18	3	
	Benzene	59.6	62.1	74.4	

	Benzene hydrogenated (butanol free basis)	34.2	22.4	3.9	
	$\frac{x(t)}{x(0)} = \frac{x(t)}{42.5}$.805	.53	.092	

Set No.	Product composition (Mole %)	Time (Minutes)			
		5	10	15	20
9	C ₆ H ₁₂	29.5	15.5	7.0	2.3
	Benzene	60.3	65.0	62.4	65.9

	Benzene hydrogenated (butanol free basis)	32.8	19.3	10.1	3.4
	$\frac{x(t)}{x(0)} = \frac{x(t)}{42.5}$.772	.455	.238	.08

C Blank Run - No Butanol in Feed

Product composition (Mole %)	Time (Minutes)				
	5	10	15	20	25
Benzene	50	37.4	37.4	33.0	29.0
$\frac{x(t)}{x(0)} = \frac{x(t)}{44}$	-	.85	.85	.75	.66

Temperature 94°C

Benzene (1) flow rate = .1 ml/min.

Hydrogen flow rate = 78 ml/min.

Weight of Catalyst = 7.63 gm.

A. Butanol Flow Rate = .02 ml/min.

Set No.	Product Composition (Mole %)	Time (Minutes)				
		5	10	15	20	25
1	C ₆ H ₁₂	61.5	53.4	50.7	40.5	30.4
	Benzene	36.0	42.8	44.8	55.0	62.0

	Benzene hydro- genated (butanol free basis)	63.0	55.5	53.2	42.5	32.9
	$\frac{x(t)}{x(0)} = \frac{x(t)}{70}$	0.9	.79	.76	.61	.47
2	C ₆ H ₁₂	60.3	52.9	48.5	42.1	27.5
	Benzene	38.2	44.6	46.2	52.2	64.3

	Benzene hydro- genated (butanol free basis)	61.2	54.2	51.2	44.7	30.0
	$\frac{x(t)}{x(0)} = \frac{x(t)}{70}$.88	.78	.73	.64	.43

B. Butanol Flow Rate 0.2 ml/min.

Set No.	Product Composition (Mole %)	Time (Minutes)				
		5	10	15	20	25
1	C ₆ H ₁₂	29.7	13.0	5.1	2.2	.7
	Benzene	58.2	75.8	65.3	58.7	57.1

	Benzene hydrogenated (butanol free basis)	33.8	14.6	7.3	3.6	1.2
	$\frac{x(t)}{x(0)} = \frac{x(t)}{44}$.77	.33	.17	.08	.03

2	C ₆ H ₁₂	34.1	17.5	6.2	3.6	0.8
	Benzene	55.3	63.2	66.3	61.8	59.7

	Benzene hydrogenated (butanol free basis)	38.2	21.7	8.6	5.5	1.3
	$\frac{x(t)}{x(0)} = \frac{x(t)}{46}$.83	.47	.19	.12	.03

C Blank Run - No Butanol in Feed

Product Composition (Mole %)	Time (Minutes)						
	5	10	15	20	25	30	35
Benzene	64.5	63	61	61	61	58	58
$\frac{x(t)}{x(0)} = \frac{x(t)}{66.5}$.985	.962	.931	.931	.931	.885	.885

Temperature 104°C

Benzene (1) flow rate = .1 ml/min.

Hydrogen flow rate = 78 ml/min.

Weight of Catalyst = 7.63 gm.

A. Butanol Flow Rate = .02 ml/min.

Set No.	Product Composition (Mole %)	Time (Minutes)				
		5	10	15	20	25
1	C ₆ H ₁₂	50	41.3	39.8	36.2	28.4
	Benzene	45.5	53.4	53.4	56.2	59.5

	Benzene hydro- genated (butanol free basis)	52.4	43.6	42.7	39.2	32.4
	$\frac{x(t)}{x(0)} = \frac{x(t)}{57}$.92	.765	.75	.688	.57
2	C ₆ H ₁₂	55.3	42.7	38.2	33.7	29
	Benzene	40.9	52.8	54.8	55.0	56.6

	Benzene hydro- genated (butanol free basis)	57.7	44.7	41.0	38.0	33.8
	$\frac{x(t)}{x(0)} = \frac{x(t)}{63}$.916	.71	.65	.603	.537

B. Butanol Flow Rate = 0.2 ml/min.

Set No.	Product Composition (Mole %)	Time (Minutes)				
		5	10	15	20	25
1	C ₆ H ₁₂	31.7	20.3	5.1	2.9	.7
	Benzene	48.1	49.4	57.0	49.6	44.8

	Benzene hydro-generated (butanol free basis)	39.8	29.2	8.2	5.5	1.5
	$\frac{x(t)}{x(0)} = \frac{x(t)}{48}$.83	.608	.171	.115	.031

2	C ₆ H ₁₂	28.5	18.8	7.1	3.0	1.5
	Benzene	48.8	53.2	54.9	54.1	48.2

	Benzene hydro-generated (butanol free basis)	36.9	26.1	12.2	5.3	3.0
	$\frac{x(t)}{x(0)} = \frac{x(t)}{48}$.765	.544	.254	.11	.06

C. Blank Run - No butanol in feed

Product Composition (Mole %)	Time (Minutes)						
	5	10	15	20	25	30	35
Benzene	78.2	78.2	79.6	78	76	76	74
$\frac{x(t)}{x(0)} = \frac{x(t)}{79}$.99	.99	1.0	.988	.962	.962	.938

Temperature 114 °C

Benzene (1) flow rate = 0.1 ml/min.

Hydrogen flow rate = 78 ml/min.

Weight of catalyst = 7.63 gm.

A. Butanol Flow Rate = .02 ml/min.

Set No.	Product Composition (Mole %)	Time (Minutes)				
		5	10	15	20	25
1	C ₆ H ₁₂	62.3	54.3	47.8	45	36.2
	Benzene	28.8	36.6	41.6	45.9	51.7

	Benzene hydro- genated (butanol free basis)	68.4	59.8	53.5	49.5	41.2
	$\frac{x(t)}{x(0)} = \frac{x(t)}{72.5}$.934	.828	.74	.68	.57
2	C ₆ H ₁₂	39.8	36.3	33.3		15.2
	Benzene	55.7	56.1	57.2		74.7

	Benzene hydro- genated (butanol free basis)	41.7	39.3	36.8		16.9
	$\frac{x(t)}{x(0)} = \frac{x(t)}{46}$.91	.855	.8		.37

B. Butanol Flow Rate = 0.2 ml/min.

Set No.	Product Composition (Mole %)	Time (Minutes)				
		5	10	15	20	25
1	C_6H_{12}	44.7	34.6	12.4	6.9	3.3
	Benzene	18.7	20.9	40.0	34.1	35.7

	Benzene hydro- genated (butanol free basis)	70.5	62.4	23.7	16.8	8.5
	$\frac{x(t)}{x(0)} = \frac{x(t)}{82.5}$.855	.756	.288	.204	.10

2	C_6H_{12}	40.2	20.8	9.3	4.1	2.8
	Benzene	29.7	24.2	40.5	34.9	32.9

	Benzene hydro- genated (butanol free basis)	57.5	34.2	18.6	10.5	7.8
	$\frac{x(t)}{x(0)} = \frac{x(t)}{70}$.823	.49	.266	.15	.11

C. Blank Run - No butanol in feed

Product Composition (Mole %)	Time (Minutes)						
	5	10	15	20	25	30	35
Benzene	87	84.5	82.5	82.5	83.5	80.3	79.3
$\frac{x(t)}{x(0)} = \frac{x(t)}{87}$	1.0	.97	.947	.947	.96	.922	.91

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The combined effect of chemisorption of butanol and condensation of butanol in the catalyst pores have been found to be responsible for the decrease in reaction rate with time. At a butanol feed rate of .02 ml/min. the probability of butanol condensation is very less, but at butanol rate of 0.2 ml/min. the butanol condensation is perhaps the factor responsible for the drop in reaction rate.

Further work in this direction can be done by choosing some other inert component and studying a larger range of temperature. It would be interesting to study a reaction in which the number of moles increased after reaction. In this study of benzene hydrogenation four moles of reactants gave one mole of product.

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APPENDIX A

EXPERIMENTAL RESULTS

Temperature 84°C

Benzene (1) flow rate = .1 ml/min.

Hydrogen flow rate = 78 ml/min.

Weight of Catalyst = 7.63 gm.

A. Butanol Flow Rate = .02 ml/min.

Set No.	Product Composition	Time (Minutes)				
		5	10	15	20	25
1	Mole % of C ₆ H ₁₂ in product	32	28	20.4	18	11
	Mole % of Benzene in product	65.9	69.3	76.6	78.5	84.5

	% Benzene hydrogenated (butanol free basis)	32.6	28.8	21	18.7	11.5
	$\frac{x(t)}{x(0)} = \frac{x(t)}{38.3}$.835	.739	.539	.480	.295
2	Mole % of C ₆ H ₁₂ in product	34.4	29	24.4	20.8	18.1
	Mole % of Benzene in product	63.1	68.3	72.6	75.5	77.9

	% Benzene hydrogenated (butanol free basis)	35.2	29.8	25.2	21.6	19.4
	$\frac{x(t)}{x(0)} = \frac{x(t)}{41}$.86	.727	.615	.527	.473

APPENDIX B

ESTIMATION OF THE EXTENT OF PORE FILLING BASED ON NORMAL BUTANOL MATERIAL BALANCE

The calculations have been performed with the following two assumptions:

- (i) Benzene and cyclohexane do not condense because of low boiling points.
- (ii) All the butanol retained in the bed fills the pore by spontaneous condensation.

Calculations:

Porosity of the catalyst pellet = 0.55

Bulk density of the catalyst bed = 1.97 gm/cc

Weight of Catalyst in the bed = 7.63 gms.

Therefore, total volume of voids = $\frac{7.63}{1.97} \times 0.55 = 2.12$ ml.

The following table has been prepared using butanol material balance:

Temperature 84°C

Set No.	Time (Mts.)	Mole % butanol in product	gm. moles of butanol in product	Cumulative gm. moles	% pore filled by butanol
1	2	3	4	5	6
Butanol Rate .02 ml/min.					
1	5	2.1	1.21×10^{-4}	1.21×10^{-4}	4.2
	10	2.7	1.54	2.75	8.25
	15	3	1.75	4.5	12.7
	20	3.5	2.06	6.56	16
	25	4.5	2.66	9.22	19.6
2	5	2.86	1.45	1.45	4.1
	10	2.7	1.57	3.02	8.15

1	2	3	4	5	6
	15	3.0	1.75×10^{-4}	4.77×10^{-4}	12.1
	20	3.5	2.06	6.83	15.9
	25	4.0	2.36	9.19	19.6

Butanol Rate 0.2 ml/min.

1	5	10.6	6.7	6.7	44.3
	10	16.5	11.2	17.9	86.8
	15	26.6	20.5	38.4	100.
2	5	10	6.3	6.3	45
	10	18.7	13.0	19.3	80.5
	15	28.	22.	41.3	100.

Temperature 94°C

Butanol Rate .02 ml/min.

1	5	2.5	1.45	1.45	4.70
	10	3.8	2.25	3.70	7.85
	15	4.5	2.66	6.36	11.4
	20	4.5	2.66	9.02	15.
	25	7.6	4.65	13.67	17.7
2	5	1.5	.86	.86	2.0
	10	2.5	1.45	2.31	8.4
	15	5.3	3.16	5.47	11.7
	20	5.7	3.42	8.89	15.
	25	8.2	5.05	13.94	17.5

1	2	3	4	5	6
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Butanol Rate 0.2 ml/min.

1	5	10.6	6.68×10^{-4}	6.68×10^{-4}	43.3
	10	19.3	13.3	19.98	96.4
	15	27.5	21.4	41.38	100.
2	5	12.1	8.78	8.78	45.3
	10	21.2	15.2	23.98	84.
	15	29.6	23.8	47.78	100.

Temperature 104°C

Butanol Rate .02 ml/min.

1	5	4.5	2.66	2.66	3.5
	10	5.3	3.16	5.82	6.91
	15	6.8	4.12	9.94	9.86
	20	7.6	4.65	14.59	12.55
	25	12.1	7.77	22.36	14.1
2	5	3.8	2.23	2.23	3.76
	10	4.5	2.66	4.89	7.34
	15	7.0	4.25	9.14	10.2
	20	11.3	7.2	16.34	11.8
	25	14.4	9.5	25.84	12.4

Butanol Rate 0.2 ml/min.

1	5	21.2	14.3	14.3	41.0
	10	30.3	24.6	38.5	77.5
	15	37.9	36.1	75.0	100.0
2	5	22.7	16.7	16.7	40.
	10	28.	22.	38.6	77.6
	15	38	34.6	73.2	100.

1	2	3	4	5	6
<u>Temperature 14 °C</u>					
Butanol Rate .02 ml/min.					
1	5	8.9	5.52×10^{-4}	5.52×10^{-4}	2.12
	10	9.1	5.66	11.18	4.62
	15	10.6	6.1	17.28	6.7
	20	9.1	5.66	22.94	9.0
	25	12.1	7.77	30.71	10.4
2	5	4.5	2.66	2.66	3.57
	10	7.6	4.65	7.31	6.3
	15	9.5	5.92	13.23	8.45
Butanol Rate 0.2 ml/min.					
1	5	36.6	32.7	32.7	33
	10	44.5	45.3	78.0	60.6
	15	47.6	51.5	129.5	85.6
	20	59.0	81.3	210.8	98.0
	25	61.0	88.5	299.3	100.
2	5	30.1	24.5	24.5	36.6
	10	39.0	36.1	60.6	68.2
	15	50.2	57.1	117.7	90.5
	20	61.0	88.5	200.2	100.0

APPENDIX C

THEORETICAL ASSESSMENT OF MAXIMUM PORE FILLED AT VARIOUS EXPERIMENTAL CONDITIONS BY USE OF KELVIN EQUATION

The Kelvin equation (9) applicable to liquid inside a capillary is as below:

$$\ln \frac{p_0}{p} = \frac{2 \gamma \cos \alpha}{rRT}$$

where p_0 = vapor pressure of liquid
 p = partial pressure of condensate in vapor phase
 γ = surface tension
 V = molar volume of the liquid
 R = gas constant
 T = absolute temperature
 r = radius of filled capillary
 α = angle of wetting between solid and liquid.

For n-Butanol, γ has been calculated by using empirical correlations (Perry's Handbook, 4th Edition, page 3-223).

The γ values calculated are as below:

Temperature, °C	γ (dyne/cm.)
84	9.6
94	9.0
104	8.5
140	7.9

The V can be assumed to be constant in the range of temperature under study.

$$\bar{V} = 58 \text{ ml/mole}$$

Also assuming the angle of wetting to be 0° , we get after substituting in Kelvin equation, and simplifying,

$$r = \frac{140 \sim}{T \ln \frac{p_0}{p}}$$

where r is in \AA and T in $^\circ\text{K}$.

Calculation of Maximum Radius of Filled Capillary for Butanol Condensation

(i) Butanol Feed Rate .02 ml/min.

	Temperatures $^\circ\text{C}$			
	84	94	104	114
p_0 (mm Hg)	198	308	458	668
p (mm Hg)	128	128	128	128
p_0/p	1.547	2.40	3.58	5.22
$\ln \frac{p_0}{p}$	0.437	.876	1.275	1.65
$r_{\max}(\text{\AA})$	8.6	3.9	2.5	1.9

(ii) Butanol Feed Rate 0.2 ml/min.

p_0 (mm Hg)	198	308	458	668
p (mm Hg)	255	255	255	255
p_0/p	1	1.21	1.80	2.62
$\ln(p_0/p)$	-	.191	.588	.964
$r_{\max}(\text{\AA})$	all filled	17.3	5.5	3.5

The average pore radius reported (10) for the catalyst is 56.2 \AA .

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